

AUTOMOBILE EXHAUST HYDROCARBON ANALYSIS
BY GAS CHROMATOGRAPHY

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Automobile Exhaust Hydrocarbon Analysis by Gas Chromatography

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► A new gas chromatographic method has been developed to analyze the complete range of hydrocarbons in both raw and highly diluted automobile exhaust gas. A commercial gas chromatograph was modified to include a separate oven for thermostating a gas sampling valve and a flow-switching valve, a subtractor column for removing the unsaturated hydrocarbons, and an adsorption column in dual arrangement with a capillary column. Sampling of exhaust gas and hydrocarbon calibration mixtures was investigated. The capabilities of the method are demonstrated with examples of analyses of exhaust gas from different engine operating modes.

AN EXTENSIVE program by both industry and government is currently under way to study and alleviate the automotive contribution to air pollution. Included in this program is a study of the influence of automobile engine operating conditions and modifications on exhaust hydrocarbon emissions. To more fully evaluate the results of this study, detailed hydrocarbon analyses are required.

Gas chromatography has become the most useful technique for analyzing the hydrocarbon portion of exhaust gas, and partial analyses have been frequently reported (6-9, 11, 16, 22). However, Hurn and coworkers (4, 7) are the only group to report reasonably complete analyses. None of these pub-

lished methods, however, was considered satisfactory for our work, in which much more complete and detailed hydrocarbon analyses were required.

The present paper describes a new method that utilizes a commercial gas chromatograph. As shown in Figure 1 the basic apparatus consists of a gas sampling valve, three columns (adsorption, capillary, and subtractor), a flow-switching valve, and a single flame ionization detector. With the flow-switching valve in the position depicted by the solid lines, the carrier gas bypasses the subtractor column and flows only through the adsorption and capillary columns. In the other valve position (broken lines), the carrier gas flows through all three columns in the order:

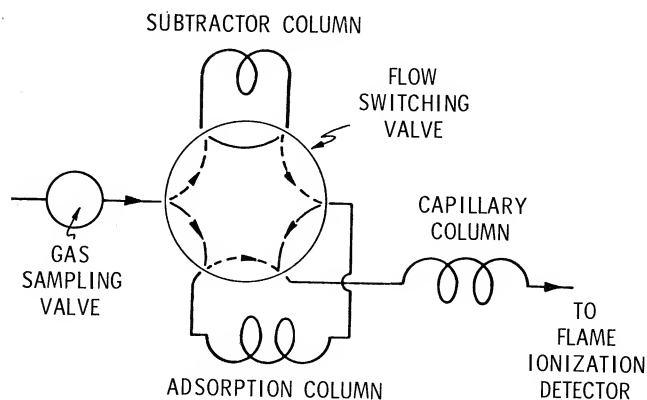


Figure 1. Basic apparatus

subtractor, adsorption, and finally capillary. Thus, in analyzing a hydrocarbon sample, the initial position of the flow-switching valve determines whether the sample is first passed through the subtractor column to remove unsaturated hydrocarbons and then into the adsorption column, or is passed directly into the adsorption column.

In the adsorption column the hydrocarbons are trapped and concentrated, while most of the inorganic gases in the sample continue through the columns and detector to vent. The C_1 and C_2 hydrocarbons are not strongly held in the adsorption column and emerge before switching the valve and back-flushing the remaining hydrocarbons into the capillary column, where they are separated. Thus, two runs are required for a complete analysis; the first for a complete sample, the second

for only the saturated hydrocarbons, and the unsaturated hydrocarbons are calculated by difference.

APPARATUS

Gas Chromatograph. A Perkin-Elmer Model 800 gas chromatograph was used for most of this work. [Some method development work and exhaust gas analyses were performed with an F and M Model 609 gas chromatograph (12).] Figure 2 shows a

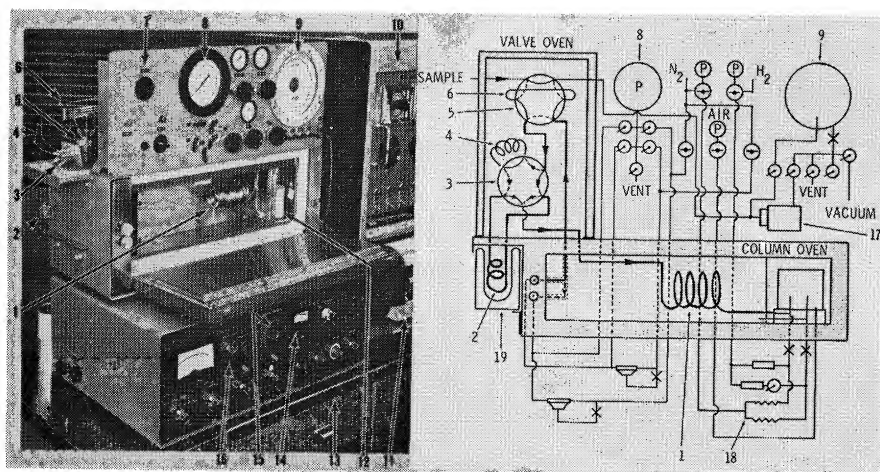


Figure 2. Gas chromatographic apparatus

- 1 Capillary column
- 2 Adsorption column
- 3 Flow-switching valve, Consolidated Electrodynamics Corp., No. 135956
- 4 Subtractor column
- 5 Gas sampling valve, The Bendix Corp. (Greenbrier Plant), Type D
- 6 Gas sample loop, 10.6 ml.
- 7 Valve oven temperature controls
- 8 Carrier gas pressure gauge, Marsh Instrument Co., Type 210
- 9 Manometer, Wallace and Tiernan, Inc., Series FA-145
- 10 Sequence controller

- 11 Dual-pen recorder-integrator, Texas Instruments, Inc.
- 12 Transite cover for detector
- 13 Instrument cart, Micro-Tek Instruments, Inc., Model GCK-453
- 14 Detector temperature controller, Assembly Products, Inc., Type 1302L
- 15 Extended column temperature graduations
- 16 Detector heater switch
- 17 Solenoid valve, Skinner Electric Valve Division, Series B
- 18 Auxiliary nitrogen lines to detector
- 19 Dewar flask, 250 ml.

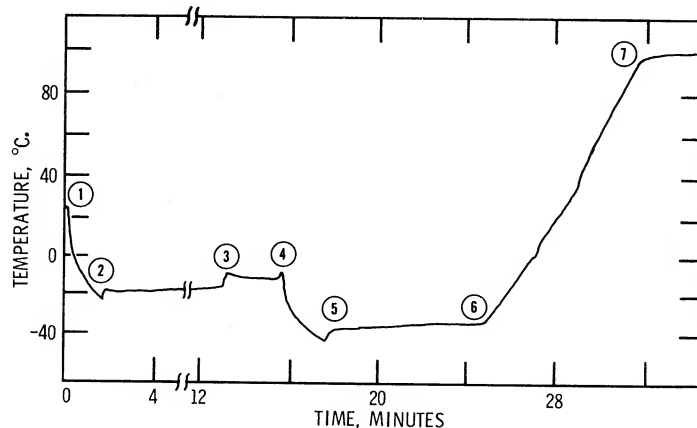


Figure 3. Subambient isothermal and temperature programmed operation of the column oven

- 1 450 ml. of chipped dry ice placed in column oven
- 2 Oven heater switch on and temperature dial set for isothermal operation at -20°C .
- 3 Fan off, oven door opened
- 4 Another 450 ml. of dry ice added
- 5 Oven heater switch on with temperature dial set at -40°C .
- 6 Temperature programmer on $20^{\circ}/\text{minute}$
- 7 Temperature programmer hold at 100°C .

photograph and flow schematic of the chromatograph as modified for exhaust hydrocarbon analysis. Above the column oven were added the controls for sample and detector gases and a valve oven for thermostating the sampling and flow-switching valves and the subtractor column. An absorption column was suspended below the valve oven so that it could be immersed in a Dewar flask. In addition, a sequence controller for automatically programming the various steps of an analysis run was constructed and is partially shown to the right of the chromatograph. The chromatograph, sequence controller, and gas cylinders were mounted on a cart to make the apparatus mobile.

Valves. The sampling and flow-switching valves must be leak-free to obtain satisfactory results. We have had the best success with pneumatically operated diaphragm valves (14). However, these valves do occasionally leak, but they are easily made leak-free again by cleaning and refitting with a new diaphragm.

Column Oven. In the analysis procedure the column oven is cooled with dry ice, then temperature programmed from -25° to 125°C . To accomplish this temperature program, the graduations on the column temperature dial (15, Figure 2) were extended below 0° to -60°C .

The oven temperature was checked for subambient isothermal and temperature-programmed operation. Satisfactory results were obtained, as shown in Figure 3. For isothermal operation at -20°C , the column oven temperature increased only 2° in 10 minutes; at -40°C , 5° in 7 minutes. When the oven was temperature programmed from -35° to 100°C , the temperature initially increased at the rate of $16.5^{\circ}/\text{minute}$ to 40°C , then changed to $21^{\circ}/\text{minute}$. Although this heating rate was not strictly linear, it was re-

producible (including the two noticeable dips in the curve).

Columns. The data for the columns are listed in Table I. The capillary column was loosely coiled stainless steel tubing of low mass to facilitate rapid heating and cooling. The adsorption column contained sections of two different packings: alumina to trap and separate the light hydrocarbons, and Apiezon-coated Chromosorb to trap and readily release the heavier hydrocarbons at either end of the column during backflushing. To maintain its low activity, the alumina was not heated above room temperature either when it was coated with sodium hydroxide or during use.

The subtractor column was a problem. A column was required that would remove all hydrocarbons except paraffins at 50° to 60° C. (sample valve oven temperature). The results of this work are compared with those of others in Table II. A packing made with mercuric perchlorate and perchloric acid was too active (branched paraffins partly removed), while that made with only mercuric perchlorate was not active enough (aromatics not completely removed). For unknown reasons a satisfactory packing could not be prepared. However, some mercuric perchlorate packing, provided by the Bureau of Mines, performed satisfactorily and was used in this work.

Detector. The original detector had to be replaced with one having a cartridge heater to avoid noise due to water condensation at the subambient column oven temperatures. The detector was insulated with a Transite cover and controlled at 100° C. by a meter-relay (14, Figure 2).

The proper gas flows to the detector were investigated for optimum response/noise. Air flow greater than 800 ml./minute gave a relatively constant response, so it was set at 850 ml./minute. Varying the total nitrogen flow showed a maximum response at 1.80 times the hydrogen flow. Although maximum response occurred at about 60 ml. hydrogen/minute, maximum response/noise was obtained in the range of 45 to 50 ml./minute. Therefore, the flows in ml./minute used throughout this work were: air, 850; hydrogen, 50 (to each jet, both were lit); carrier nitrogen, 5.5; and auxiliary nitrogen, 85.

The response of the detector was checked with the hydrocarbons listed in Table III. The responses per carbon atom range from 99 to 105% compared to propane. Since this range is within experimental error, the detector was considered to have a uniform hydrocarbon response on a carbon basis. The response for propane was 0.45 coulomb/mole, which is about double the minimum response quoted for the instrument (17).

The hydrocarbons listed in Table III were purchased from The Matheson Co., Inc., individually blended in nitrogen. Their concentrations were established by comparing them with standard mixtures calibrated by the method of Heaton and Wentworth (6).

Table I. Column Data

Type	Subtractor ^a	Adsorption	Capillary
Tubing: length, inches	10	40	150 ft.
i.d., inches	0.093	0.042	0.010
o.d., inches	0.125	0.062	0.020
Support: name	GC-22	Alumina	Chromosorb
or grade		F-10	P
adsorbent: supplier	Coast Engineering	Alcoa	F & M
mesh	50-60	80-100	80-100
Coating: name	Hg(ClO ₄) ₂	NaOH	Apiezon J
			DC 200
			Silicone
Packing: concn. wt. %	40	10	6
wt., mg.	433	416	169
length, inches	6	18	16 ^b

^a Packing received from Bureau of Mines.

^b Eight inches of packing at both ends of the tubing. Tube ends closed with 3-inch lengths of 20- and 28-gauge tubing.

Table II. Comparison of Mercury Subtractor Column Performance

Reference	mmoles/100 grams support		Support	Operating temp., ° C.	Removed ^a , %	
	Hg(ClO ₄) ₂	HClO ₄			Paraffins	Aromatics
(3)	69	138	Firebrick 40-60	100	0	partly
(18)	69	138	...	82	0	0
(10)	83	55	Chromosorb P 28-35	>82 60	partly 0	not tested
This work	69	138	Chromosorb P 100-120	24 60	0 branched, partly	100 100
This work	150	none	Firebrick C-22 100-120	50	0	partly
This work	100	none	Coast Engineering GC-22 ^b 50-60	50	0	100
(4)	100	none	Coast Engineering GC-22 42-60	24	0	100

^a Olefins and acetylenes 100% removed.

^b Packing received from Bureau of Mines.

ANALYSIS METHOD

Procedure. The chromatograph was prepared for analysis by cooling both the adsorption and capillary columns with dry ice; the adsorption column with dry ice-trichloroethylene in a Dewar flask, and the capillary column with chipped dry ice in a wire basket in the column oven. If the unsaturated hydrocarbons were not to be removed, the flow-switching valve was initially positioned so as to bypass the subtractor column. In all the work reported here, a 10.6-ml. loop was used on the gas sampling valve.

The sample was injected into the adsorption column, where all the hydrocarbons were trapped and separated from the light inorganic gases. Methane was not strongly held and when its peak started to appear, the Dewar flask was removed to allow the adsorption column to slowly warm in the room air. After ethane and ethylene had entered the capillary column (about 3.5 minutes), the valve was switched to backflush the hydrocarbons from the packed column into the capillary column. At the same time the adsorption column was warmed to room temperature with a water bath

Table III. Relative Response of Some Hydrocarbons

Hydrocarbon	Concn., p.p.m.	Response/ carbon (propane = 100)
Methane	145	102
Ethane	108	100
Ethylene	100	101
Acetylene	101	104
Propane	104	100
Propylene	102	105
i-Butane	153	99
n-Butane	103	99
n-Hexane	100	100

to promote the backflushing operation. After the C₄ hydrocarbons had been eluted, the capillary column was heated at 10° C. per minute, starting at -25° C. and stopping at about 125° C., and the run continued until no more peaks appeared. A run usually lasted from 20 to 22 minutes.

If the unsaturated hydrocarbons were to be removed, the switching valve was first positioned so that the carrier gas flowed through the subtractor column. The procedure was the same for all runs, with the exception of the initial positioning of the switching valve.

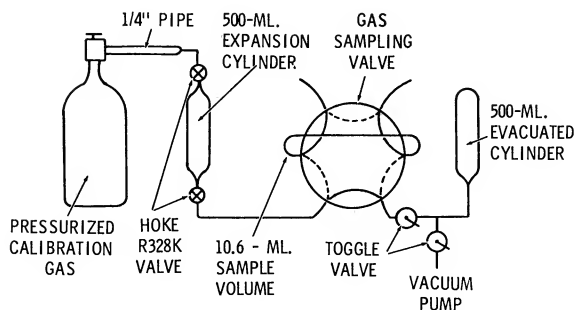


Figure 4. Schematic of sampling system for pressurized calibration gases

Method Development. The above procedure has several improvements over the original method (13). Originally the light hydrocarbons to *n*-butane were eluted at room temperature, then the adsorption column was heated with almost boiling water to promote the backflushing of the heavier hydrocarbons. The use of boiling water was objectionable, and even at this temperature, the heavier hydrocarbons were occasionally not backflushed

sharply enough, as indicated by the separations obtained with the capillary column. A significant improvement was made by advancing the valve switching time for backflushing from approximately the appearance of *n*-butane to before ethane. Not only was the separation of the heavier hydrocarbons improved in the capillary column, but it was also discovered that the C_3 and C_4 hydrocarbons were much more sharply separated in the

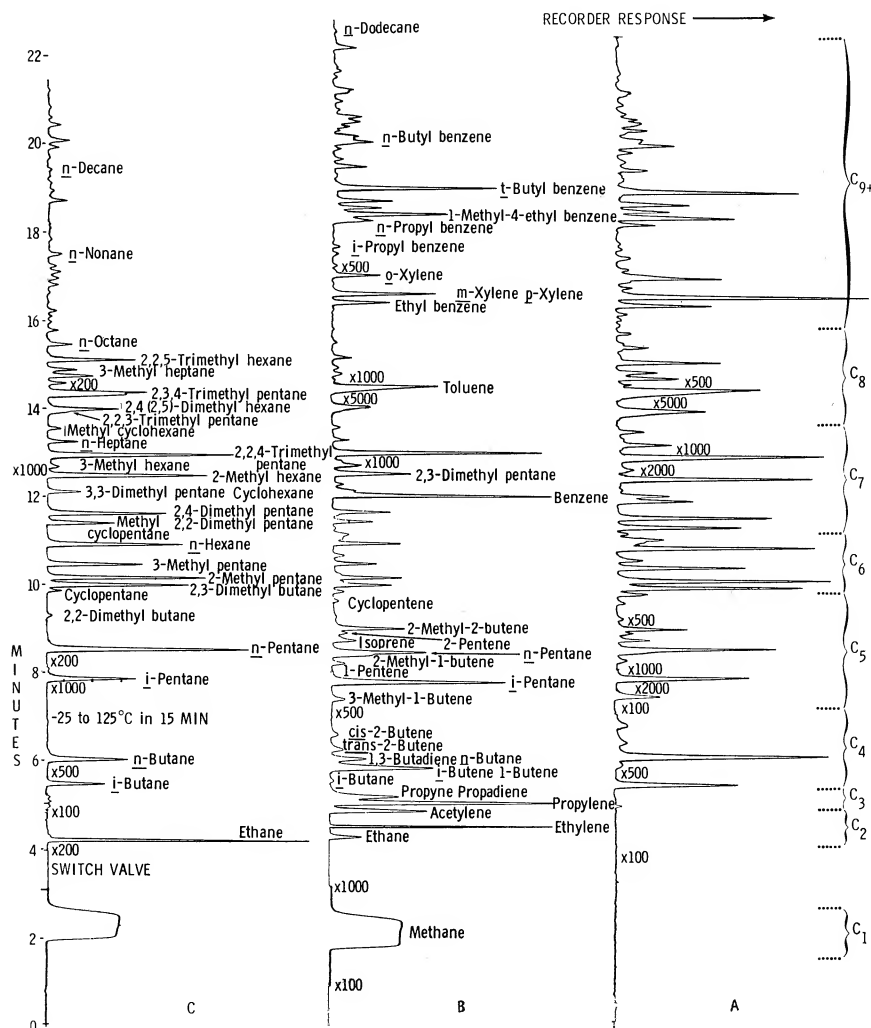


Figure 5. Chromatograms showing fuel and exhaust hydrocarbon separations

- A Indolene 30 fuel, complete sample
- B Exhaust gas from modified engine, 15-30 m.p.h., complete sample
- C Same exhaust gas as B, unsaturated hydrocarbons removed

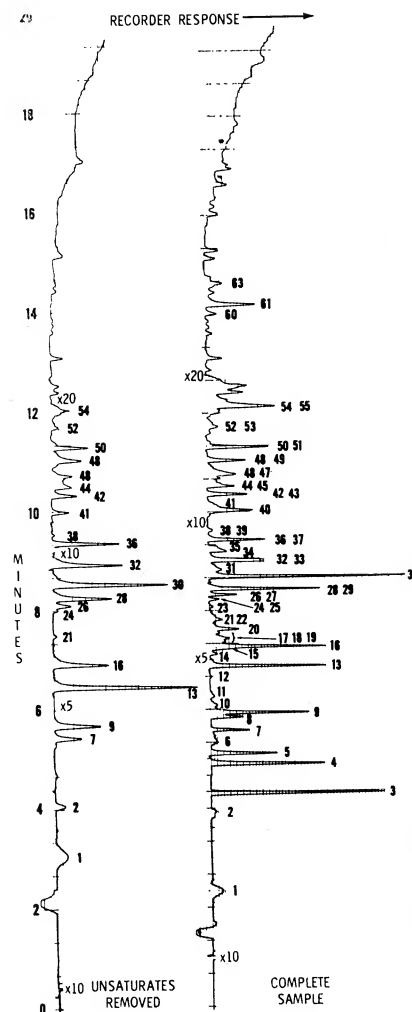


Figure 6. Chromatograms of smog chamber gas

See Table V for peak identification

backflush mode. Methane, ethane, and ethylene were foreflushed at subzero temperatures; then the backflushing of all the remaining hydrocarbons could be promoted with room temperature water.

Another improvement involved reducing the activity of the alumina in the adsorption column so as to still separate the light hydrocarbons, yet readily release the heavier hydrocarbons during backflushing. Alumina was used because it adsorbs carbon dioxide (5), which otherwise interferes with the ethane-ethylene separation. Of the various surface modifiers suggested in the literature, sodium hydroxide (19) proved to be satisfactory. Of the others, water (20) was too volatile and the activity of the alumina kept changing, and silicone oil (20) did not adequately separate the light hydrocarbons. Apiezon C (5% coating) was used with the original method, but extraneous peaks appeared when the alumina was heated with boiling water during backflushing.

SAMPLING

Liquids. Liquid samples, which were mainly gasolines, were more satisfactorily sampled as diluted vapor

than as a liquid with a syringe. The syringe did not reproducibly inject the volatile gasolines, and an inlet stream splitter in the cold column oven had to be wrapped with heating wire and insulated to avoid condensing the sample.

Vapor sampling with the gas sampling valve was accomplished by first syringe-injecting the liquid into an evacuated 500-ml. stainless steel cylinder fitted with a septum. Very volatile samples, such as a cold-trapped condensate, were introduced with only a needle that had been cooled with liquid nitrogen and then dipped into the dry ice-cooled liquid. The heated cylinder containing stainless steel balls was then pressurized to about 2 atm. nitrogen, and shaken to completely mix the contents. This method enables the exact repetition of sample size, but has the disadvantage of possible contamination or adsorption in the cylinder.

Calibration Gases. Pressurized gas mixtures were sampled with the apparatus shown in Figure 4 to avoid fractionating the mixture. A small volume of the high pressure gas was rapidly expanded into a 500-ml. cylinder, from which a sample could be withdrawn at a low pressure. Calibration mixtures as complex as the one containing 21 hydrocarbons from methane to *p*-xylene in 500-p.s.i. nitrogen (13) have been sampled without change by this procedure.

In addition to preventing fractionation, the apparatus of Figure 4 was also used to investigate hydrocarbon adsorption in the sampling system. For calibration mixtures, two methods of filling the sample loop were studied: evacuation and throughflow. In the first method, just enough sample passed through the inlet tube to fill the evacuated loop to atmospheric pressure. In the second, the sample flowed through the loop into an evacuated 500-ml. cylinder. If hydrocarbons were adsorbed, the concentration of the sample in the loop would be low by the evacuation method and high by the flow method.

No difference between the two methods was found. With the apparatus at 24° C., the peak area for 133-p.p.m. toluene was 0.56 ± 0.02 coulomb/mol. for 14 runs. Even heating the expansion cylinder and inlet line to 80° C. had no effect, indicating no adsorption and subsequent desorption of the toluene. However, the author has had discussions with other researchers who have found the flow method to give high results, so this method should be checked with a particular sampling system before being used.

Exhaust Gas. Exhaust gas from a single-cylinder engine was sampled both directly into the chromatograph and into 500-ml. stainless steel cylinders. A comparison of the results for these two

sampling methods showed that the sample cylinders had to be heated to 115° C. to obtain complete hydrocarbon recovery. Below this temperature the peak areas of the C_{9+} aromatics were smaller for the cylinder-stored samples than those for the directly sampled exhaust gas, indicating some adsorption of these heavier hydrocarbons in the cylinders.

The stability of cylinder-stored samples was influenced by engine air/fuel. At an air/fuel of 13.0, the olefin and aromatic concentrations remained constant for at least an hour before starting to decrease slightly. At an air/fuel of 16.2, however, the olefin and aromatic concentrations in the raw exhaust decreased about 12% in the first half hour, but this was improved to only a 4% change by diluting the exhaust ninefold with nitrogen. No change in paraffin concentrations was noted.

Sampling of exhaust gas was also investigated by collecting the exhaust from a V-8 engine in a Mylar bag for three 7-mode cycles (2). In this case the chromatograph could not be moved next to the automobile for direct sampling and a reference analysis, so a portion of the bag sample was diluted 25-fold with nitrogen in a stainless steel cylinder to minimize hydrocarbon reactions. An analysis of both the raw and diluted exhaust gas samples 24 hours later showed no difference (other than dilution) for the C_1 to C_8 hydrocarbons,

Table IV. Automobile Exhaust Gas Analysis

Hydrocarbon concn., p.p.m. (wet exhaust basis), and % concn. reduction from standard (S) to modified (M) engine (values adjusted for air dilution). Modifications include air injection system, leaner carburetor, and 10° spark retard at closed throttle.

	Carbon no.	Acceleration, 15-30 m.p.h.			Cruise, 30 m.p.h.			Idle			Deceleration 50-20 m.p.h.		
		S	M ^a	Red., %	S	M	Red., %	S	M	Red., %	S	M	Red., %
Paraffins	1	97	61	37	112	36	68	650	263	60	1242	13	99
	2	20	14	30	22	8.5	60	21	11.5	44	282	5.5	98
	4	14	10.3	27	11	8.0	29	28	7.3	74	439	24	94
	5	32	23	29	26	17	36	60	17	72	797	47	94
	6	21	14	32	17	10.6	36	41	11.2	73	490	27	94
	7	18.5	13	31	15	9	42	38	10.3	73	411	22	95
	8	65	48	27	52	34	34	138	41	70	1350	87	93
	9+	6.4	2.6	59	2.5	1.1	56	19	5.3	72	167	9.6	94
		274	186	32	257	124	52	995	366	63	5178	235	96
Olefins	2	118	103	12	133	93	30	188	81	57	1030	39	96
	3	72	59	18	70	51	28	67	33	51	584	21	96
	4	47	35	26	51	30	42	54	21	62	477	20	96
	5	21	17	19	21	17	19	33	9.6	71	354	18	95
	6	8.3	7.7	8	10	7.0	31	16	5.2	69	129	10	92
	7	1.9	1.1	38	2.6	1.4	45	5.1	0.9	83	34	3.1	91
		268	223	17	287	199	31	363	150	59	2608	111	96
Acetylenes	2	57	36	37	69	35	49	308	96	69	1235	14	99
	3	11	7	34	10	9	16	8	4	48	54	3	96
		68	43	37	79	44	44	316	100	68	1289	17	99
Aromatics	6	20	14	31	17	12	31	35	20	43	185	8.8	95
	7	84	60	29	81	49	40	158	55	65	1380	80	94
	8 ^b	26	18	31	25	14	44	50	20	60	371	21	94
	9+ ^b	36	29	20	34	22	35	78	23	71	375	32	91
		166	121	27	157	97	38	321	118	63	2311	142	94
Total		776	573	26	780	464	40	1995	734	63	11386	505	96
Average carbon no. ^c		4.40	4.40		4.14	4.35		3.57	3.40		4.87	5.95	

^a Chromatograms for this analysis shown in Figure 5.

^b Includes C_{9+} olefins. These olefins comprised about 5% of the total olefins when an olefin subtractor column, $HgSO_4-H_2SO_4$ (8), was used on exhaust from another engine.

^c Av. carbon number = $\frac{\text{total p.p.m. carbon}}{\text{total p.p.m. hydrocarbon}}$

but only half the expected amount of C_{9+} hydrocarbons was found in the diluted sample. This loss may have been due to baseline drift interference or adsorption effects at the high dilution. Smith, Rose, and Kruse (21) found the total hydrocarbon concentration in raw auto exhaust decreased about 10% in 1 hour, but this could be stabilized by a four-fold dilution with nitrogen.

One factor that may influence the decrease in exhaust gas stability with increasing air/fuel is the concentration of the oxides of nitrogen, NO_x , which greatly increases at leaner air/fuel ratios (15). For example, the NO_x concentration in exhaust gas for the single-cylinder engine at an air/fuel of 13.0 was 740 p.p.m., but at 16.2 was 2250 p.p.m. The NO_x concentration in the exhaust gas from the V-8 engine (average air/fuel between 13 and 14) was 1320 p.p.m. Thus the least stable exhaust gas (air/fuel, 16.2) had the highest NO_x concentration. Although it appears that the oxides of nitrogen react with the hydrocarbons, the actual reason for the hydrocarbon loss is unknown.

RESULTS

Exhaust Gas. To illustrate the versatility of this method, results for the analysis of exhaust gas at four different engine modes (idle, cruise, acceleration, and deceleration) are listed in Table IV. These analyses, which are grouped by hydrocarbon type and carbon number, include not only raw exhaust but also exhaust gas that had been diluted and reacted with air injected into the exhaust manifold (1). The data show the marked influence that engine operating mode had on both the hydrocarbon concentrations for the standard engine and on the effectiveness of the modifications in reducing the hydrocarbon concentrations. Deceleration produced the highest concentrations and the greatest reductions, followed by idle, cruise, and acceleration. The total hydrocarbon concentrations for these samples range from over 11,000 p.p.m. down to 230 p.p.m. (deceleration uncorrected for air dilution).

An example of the chromatograms for one of these samples (acceleration) and for the fuel is shown in Figure 5. The fuel contained 60% paraffin, 10% olefin, and 30% aromatic measured by fluorescent indicator adsorption analysis. The chromatograms illustrate that, even at the lower exhaust hydrocarbon concentrations, the peaks were well defined and free from any interference from baseline drift or noise.

Atmosphere Analysis. Automobile exhaust gas diluted to approximately atmospheric concentration in a smog chamber has also been successfully analyzed. Figure 6 shows the chromatograms, and Table V lists the analysis results for such a sample. This sample contained a total of only 2.27-p.p.m. hydrocarbon, and concentrations as low as 1 p.p.b. were measured. To determine the C_{8+} hydrocarbons at this dilution required a correction for baseline drift. The hydrocarbons were identified by retention times as previously reported (12).

Table V. Analysis of Dilute Exhaust Gas from the Smog Chamber

Peak no., Fig. 6	Paraffins	Hydrocarbon concn., p.p.b.	Peak no., Fig. 6	Olefins	Hydrocarbon concn., p.p.b.
1	Methane	210	3	Ethylene	345
2	Ethane	33	5	Propylene	103
7	<i>i</i> -Butane	45	8	<i>i</i> -Butene	65
9	<i>n</i> -Butane	87		1-Butene	
13	<i>i</i> -Pentane	92		1,3-Butadiene	
16	<i>n</i> -Pentane	42	10	<i>t</i> -2-Butene	15
21	2,2-Dimethylbutane	1	11	<i>c</i> -2-Butene	9
24	Cyclopentane	3	12	3-Methyl-1-butene	1
26	2,3-Dimethylbutane	9	14	1-Pentene	3
28	2-Methylpentane	36	15	2-Methyl-1-butene	14
30	3-Methylpentane	65	17	2-Methyl-1,3-butadiene	11
32	<i>n</i> -Hexane	37	18	<i>t</i> -2-Pentene	12
36	{Methyl cyclopentane	57	19	<i>c</i> -2-Pentene	5
	{2,2-Dimethylpentane		20	2-Methyl-2-butene	19
38	{2,2,3-Trimethylbutane	5	22	{3,3-Dimethyl-1-butene	10
	{2,4-Dimethylpentane		{1,3-Pentadiene		
41	{Cyclohexane	13	23	Cyclopentene	1
	{3,3-Dimethylpentane		25	4-Methyl-1-pentene	0
42	{2-Methylhexane	23	27	2,3-Dimethyl-1-butene	1
	{2,3-Dimethylpentane		29	4-Methyl-2-pentene	0
44	3-Methylhexane	27	31	{1-Hexene	11
46	{2,2,4-Trimethylpentane	26		{2-Methyl-1-pentene	
48	{3-Ethylpentane	27	33	2-Ethyl-1-butene	0
	<i>n</i> -Heptane		34	{2-Hexene	16
50	{Methylcyclohexane	29	35	{3-Hexene	
	{2,2-Dimethylhexane		37	2-Methyl-2-pentene	
52	{2,2,3-Trimethylpentane	8	39	3-Methyl-2-pentene	1
	{2,5-Dimethylhexane			{2,3,3-Trimethyl-1-butene	
54	{2,4-Dimethylhexane	24	43	{2,3-Dimethyl-2-butene	5
	{3,3-Dimethylhexane			Cyclohexene	
	{2,3-Dimethylhexane		45	{5-Methyl-2-hexene	4
	{2,3,3-Trimethylpentane			{3,4-Dimethyl-2-pentene	
	{2,3,4-Trimethylpentane	60	47	1-Heptene	13
	Other C ₈ and C ₉₊		49	3-Heptene	0
	Total paraffins		51	2-Heptene	10
	959		53	{2,4,4-Trimethyl-2-pentene	8
Aromatics		{4-Methylcyclohexene			
		{3-Methylcyclohexene			
40	Benzene	45	Total olefins		702
55	Toluene	48	Acetylenes		
60	Ethylbenzene	17	4	Acetylene	265
61	<i>m,p</i> -Xylenes	78		6	Propyne
63	<i>o</i> -Xylene	26	Total acetylenes		295
	C ₉₊ aromatics	100	Total hydrocarbons		2270
C ₈₊ olefins	314				
Total aromatics					

The detail in which the results are reported in Table IV indicates the excellent separations and extreme sensitivity that are possible. This detail is valuable for following the change in individual hydrocarbon concentrations as the dilute exhaust gas is irradiated in the smog chamber.

ACKNOWLEDGMENT

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LITERATURE CITED

- (1) Brownson, D. A., Stebar, R. F., Soc. Auto. Eng. Meeting, Chicago, Ill., May 17-21, 1965.
- (2) California Motor Vehicle Pollution Control Board, "California Test Procedure and Criteria for Motor Vehicle Exhaust Emission Control," Revised Jan. 23, 1964.
- (3) Coulson, D. M., *ANAL. CHEM.* **31**, 906 (1959).
- (4) Ferrin, C. R., Chase, J. O., Hurn, R. W., in "Gas Chromatography," N. Brenner, J. E. Callen, M. D. Weise, eds., p. 423, Academic Press, New York, 1962.
- (5) Greene, S. A., Pust, H., *ANAL. CHEM.* **29**, 1055 (1957).
- (6) Heaton, W. B., Wentworth, J. T., *Ibid.*, **31**, 349 (1959).
- (7) Hurn, R. W., *et al.*, *Proc. Am. Petrol. Inst. III* **42**, 657 (1962).
- (8) Innes, W. B., Bambrick, W. E., Andreatch, A. J., *ANAL. CHEM.* **35**, 1198 (1963).
- (9) Jones, J. L., *et al.*, *J. Air Pollution Control Assoc.* **13**, 73 (1963).
- (10) Martin, R. L., *ANAL. CHEM.* **34**, 896 (1962).
- (11) Mayrsohn, H., O'Neal, Q., Division of Water and Waste Chemistry, 148th Meeting, ACS, Chicago, Ill., September 1964.
- (12) McEwen, D. J., *ANAL. CHEM.* **35**, 1636 (1963).
- (13) *Ibid.*, **36**, 279 (1964).
- (14) McEwen, D. J., *J. Chromatog.* **9**, 266 (1962).
- (15) Nebel, G. J., Jackson, M. W., *J. Air Pollution Control Assoc.* **8**, 213 (1958).
- (16) Neligan, R. E., Mader, P. P., Chambers, L. A., *Ibid.*, **11**, 178 (1961).
- (17) Perkin-Elmer Corp., Norwalk, Conn., "Model 800 Instrument Manual," p. 5, May 1962.
- (18) Rowan, R. Jr., *ANAL. CHEM.* **33**, 658 (1961).
- (19) Scott, C. G., in "Gas Chromatography, 1960," R. P. W. Scott, ed., p. 317, Butterworths, Washington, 1960.
- (20) Scott, C. G., *J. Inst. Pet.* **45**, 118 (1959).
- (21) Smith, R., Rose, A. H., Jr., Kruse, R., *Int. J. Air Water Poll.* **8**, 427 (1964).
- (22) Stephens, E. R., Pattison, J. N., Division of Water and Waste Chemistry, 144th Meeting, ACS, Los Angeles, Calif., April 1963.

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